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(57) Abstract

A method of making a composition for forming an article having increased barrier properties to gases and vapours is disclosed. The method comprises the step of mixing together a polar resin with a high purity talc filler. The talc filler has a percentage reflectance at 500 nm of at least 85 %, and is capable of delaminating when the composition is subjected to high shear. Preferably, the aspect ration of the filler increases, ideally by a factor of at least two, as it breaks down into platelets. Also disclosed are compositions made according to the method of the invention, and articles manufactured from such compositions.

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BARRIER COMPOSITIONS AND ARTICLES PRODUCED THEREFROM

Field of the invention

This invention concerns thermoplastics compositions and articles made therefrom having gas and vapour barrier properties.

Background of the invention

Thermoplastic materials are widely used in packaging because of their low cost and ease of forming into a variety of shapes. However, most thermoplastics materials suffer from the disadvantage of providing only a relatively poor barrier to gases and vapours. Poor gas barrier is a particular disadvantage in packaging oxygen-sensitive materials such as foodstuffs which are to be stored unrefrigerated. Poor vapour barrier properties are a disadvantage when packaging materials which are sensitive to moisture vapour, for example foodstuffs and confectionery which deteriorate when they become damp, and there are also disadvantages when the packaged material includes flavouring components which diffuse through the packaging material with consequent loss of flavour.

A number of attempts have been made at improving the gas barrier properties of thermoplastics materials. GB-A-1,136,350, for example, proposes the use of circular platelike fillers with a ratio of diameter to thickness between 20:1 and 300:1 and a diameter of at most 40μm in polyolefin polymers selected from polyethylene, polypropylene, ethylene-containing copolymers containing at least 50 mole percent of ethylene, and polystyrene, the preferred amount of filler being 0.1 to 50wt% of the total weight of filled polymer. Such filled compositions are proposed to be used to manufacture films, for example for food packaging.

US-A-3,463,350 is concerned with the production of moulded containers for packaging foodstuffs, the containers being made from mixtures of high density polyethylene (HDPE) and mica particles, for example by compression or injection moulding. Such containers are said to reduce the discoloration of canned corned beef as caused by oxygen compared with the use of similar containers made of HDPE filled with glass fibre or titanium dioxide instead of mica.

It has also been proposed in US-A-4,528,235 to incorporate platelet filler particles with an average equivalent diameter of from 1 to 8μm, the maximum diameter being 25μm, and thickness of less than 0.5μm, into HDPE having a melt index of from 0.01 to 1.0g/10 minutes at 190°C as measured by ASTM D-1238, to produce films having a thickness of from 10 to 100μm, with the intention of increasing the oxygen barrier of the films compared with films formed from unfilled HDPE.

Despite the apparent improvements in oxygen barrier resulting from these various hitherto proposed methods using lamellar fillers to impart oxygen barrier properties to polyolefins, even higher oxygen barrier properties have been sought. Thus US-A-4,536,425 proposes increasing the gas barrier properties of polar thermoplastics resins, for example alkylene terephthalates, by blending the resins with mica flakes having a plurality of platelets using a shear force which effects delamination of the mica platelets and thereby results in a substantial increase in the aspect ratio of the flakes. Delamination of the mica flakes is said to occur as a result of shear force generated during mixing of the resin with the mica being transferred to the mica flakes due to chemical bonding of silanol groups on the surface of the flakes to hydroxyl and carboxyl groups formed in the resin as a result of hydrolysis of ester groups in the resin at the temperature involved.

Summary of the invention

According to the present invention there is provided a method of making a composition for forming an article having increased barrier to gases and/or vapours, the method comprising the step of mixing a polar thermoplastic resin together with a high purity talc filler having a percentage reflectance at 500 nm of at least 85%, the talc filler being capable of delaminating when the composition is subjected to high shear.

Preferably the delamination increases the aspect ratio of the filler as it breaks down into platelets.

Compositions in accordance with the present invention have been found to provide a good barrier not only to oxygen but also to flavour molecules. A particularly preferred use of compositions manufactured in accordance with the present invention is as a flexible polymer layer forming part of a laminate having barrier properties. A typical multi-layer structure toothpaste tube includes a layer of a polymer having barrier properties, for example an ethylene/vinyl alcohol copolymer. Ethylene vinyl alcohol is expensive and the inclusion of a filler allows the cost of the barrier layer to be reduced, without any reduction in its barrier properties. Where a multilayer structure in the shoulder of a tube container is not a practical solution to manufacturing a tube, such as in the laminate tube process practised by many manufacturers, it is sometimes necessary to add an additional separate moulded insert and assemble this into the inside of the shoulder in order to provide acceptable levels of flavour retention in the product which is close to the shoulder area. These moulded inserts are typically manufactured in PBT or PET resins and the moulding and insertion of the barrier as well as the cost of the resin adds considerably to the cost and complexity of the tube.

Polar thermoplastic resins include: ethylene vinyl alcohol (EVOh); polyamides such as nylon 6 and nylon 66, amorphous polyamides, nylon MxD6; polyketones (preferably aliphatic), cellulose; polyesters such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate); polyvinyl alcohol, polyvinylidene chloride, polyacrylonitrile, and liquid crystal polymers e.g. Vectran (trade mark).

The talc filler can be any of a variety of talcs that delaminate under shear, when the filler is blended with the polar resin, and/or when the mixture of filler and resin is subjected to processing.

The talc should have a structure consisting of platelets both before and after being subjected to high shear. As will be appreciated, in addition to delamination, subjecting such fillers to high shear also tends to reduce their effective diameter. However, despite a reduction in the effective diameter of the filler particles, high shear generally results in an increase in the aspect ratio of the individual filler particles.

Talc, being a naturally occurring hydrated magnesium silicate, is available in a variety of grades of greater or lesser purity. It has surprisingly been found that the ease of increasing the aspect ratio of talc when it is subjected to high shear in a polar thermoplastic resin appears to increase as the level of impurities within the talc decreases. Thus not only does it appear easier to delaminate the platelets of the talc, but the platelets themselves apparently resist fracture, when the level of impurities is low.

According to another aspect of this invention there is provided a composition for forming an article having increased barrier to gases and/or vapours, the composition comprising a substantially polar thermoplastic resin filled

with platelets of high purity talc having a percentage reflection of at least 85% at 500nm. Preferably the talc filler has an aspect ratio of at least 5 before processing.

Delamination of the talc has usually been found to occur if the percentage reflection of the talc is at least 85%, and a significant increase in the aspect ratio of the talc particles usually occurs if the percentage reflection of the talc is at least 87%.

Whatever the mechanism by which the aspect ratio of some talcs is increased to a particularly high degree when they are subjected to high shear in polar thermoplastic resins, it has surprisingly been found that the talcs which are of use in the invention, (i.e. those having a high percentage of reflection) are those talcs which delaminate relatively easily and resist fracture, that is they resist reduction in their diameter when sheared. The delamination of the talc is also associated with the CIE (Commission International d'Eclairage) whiteness index.

The CIE whiteness index values were determined for compositions containing 15 percent by weight of talc in high density polyethylene with no other filler present, the determination being in reflectance mode with UV light included and specular reflection excluded, the observer angle being 10° and the samples being backed by a white tile. It has been found that talc (e.g. Magsil osmanthus) having the required delamination properties produces a CIE whiteness index of at least 45, preferably at least 50 and typically about 56, whereas talc which was not suitable for the present invention (e.g. Luzenac 8218) produces a CIE whiteness index of less than 40.

Purer grades of talc are therefore generally preferred since it would appear that they lead to compositions in accordance with the invention which not only have good barrier properties but also high degrees of whiteness without the necessity to include significant amounts a white

pigment such as titanium dioxide.

Particularly preferred grades of talc for use in the present invention are sold by Richard Baker Horizon Group, England, under the Trade Mark "Magsil", especially preferred grades being Magsil osmanthus and Magsil 2628.

Before being subjected to high shear, the filler particles preferably have an average particle diameter of not more than 100μm, more preferably not more than 50μm, and most preferably not more than 20μm. Preferably the talc should have a 50% average particle size of about 17μm, with 70% of the particles having a size of between 10-25μm. The particle thickness of the filler can also vary over a wide range, but it is preferably less than 10μm before being subjected to high shear, and more preferably less than 5μm.

The particularly preferred grade of talc referred to above as Magsil osmanthus typically has an average particle diameter of about 20μm and a thickness of about 2.5μm before being subjected to high shear.

The filler used in accordance with the present invention is reduced in thickness as a result of high shear, and this generally increases the aspect ratio of the filler particles even though thickness reduction is usually accompanied by a reduction in the average diameter of the filler particles. A typical increase in the aspect ratio of the filler particles is by a factor of at least two, and preferably by at least three. For example, filler particles with an original aspect ratio of about 7 have had their aspect ratio increased to about 15 or more, for example to in excess of 21. Preferably the talc platelets after processing have an average size of between 2-10μm and preferably 4-8μm with an average aspect ratio of at least 15.

The high shear to which the filler particles are subjected in accordance with the present invention can be applied by various methods. It is particularly preferred to apply high shear during compounding prior to forming desired articles so that delamination of the filler particles is effected before forming the desired articles. Further delamination can also be effected during the forming step. It is generally preferred, however, to effect most of the delamination during the compounding operation, the preferred compounding operation being the use of a twin screw extruder or a Banbury mixer.

Preferably the composition contains between 5-30% by weight of talc filler, preferably 10-20% by weight of talc.

In addition to delamination of the filler particles, it is generally preferred to effect forming of the filled resin under conditions which cause the filler particles to become oriented such that their larger face is substantially aligned with the surface of the mouldings. This may be effectively achieved by extruding the filled resins which may also effect delamination of the filler particles, thereby leading to an especially good barrier to flavour molecules. The compositions can be extruded in various forms, for example as films or tubes, having increased barrier properties. They can be extruded as a single web, or they can be coextruded with other layers on one or other side of a core layer formed from a composition in accordance with the present invention. The co-extrusion may be in the form of tubes, or a multilayer strip. Films or tubes produced from compositions in accordance with the present invention can be used to form the body portions of toothpaste tubes, and a particularly preferred combination is of a tubular body portion made from a composition in accordance with the present invention, and a shoulder portion made from a composition in accordance with the present invention.

Although of particular value in the production of toothpaste tubes, it will be appreciated by those skilled the art that the end use of the tubes can be for any purpose. Uses exploiting the particularly good barrier properties of compositions in accordance with the present invention are particularly preferred, especially after a forming operation in which the filler particles become aligned parallel to the surface of the formed articles produced therefrom.

Detailed description of preferred embodiments

The invention is hereinafter described in more detail by way of example only, with reference to the following examples and tests.

Samples of different talc fillers were submitted for reflectance spectroscopy. Each sample was packed into a steel trough. The trough was mounted on the sample port of a 60mm diameter barium sulphate coated integrating sphere. The sphere was configured such that both the specular and diffuse components of the reflected radiation were collected. Spectra were recorded from 250 to 850nm using a Perkin Elmer Lambda-9 spectrometer. The reference material used was a Russian Opal plate, reference DT86, which had been calibrated for absolute % reflection between 380 and 1200nm by the National Physical Laboratory (U.K.). In order to determine the absolute reflectance of the talc sample it is necessary to correct for the imperfect reflection of the Russian Opal. Results of these calculations at two wavelengths are presented below:

TALC FILLER	%R ABSOLUTE	
	380nm	550nm
Magsil Sapphire	76.04	81.99
Norwegian Talc IT Extra	84.19	87.63
Magsil Osmanthus	79.15	89.26
Magsil 2628	81.99	87.63

A number of different grades of talc and a single grade of mica (Microfine P66) were each blended with melts of EVOh or PET in a weight ratio of 15 parts of filler to 85 parts of polymer using a twin screw extruder, the mixture being subjected to high shear during mixing prior to extrusion, the mixture being then extruded and cut into pellets.

The same technique was used for making pellets for the CIE index determinations.

The resulting pellets were then compression moulded for test samples for CIE whiteness index determinations using a Macbeth spectrophotometer. The moulded samples were in the form of plaques which were compression moulded at 150°C under a pressure of 0.39 tonnes per cm^2 for 5 minutes. Magsil osmanthus produced a CIE whiteness index of 56, and Norwegian Talc a CIE index of 42.

The aspect ratios of the talc particles were measured before mixing and in the pellets after extrusion and cutting.

The mean diameter and thickness of the talc particles were measured by scanning electron microscopy of either the talc used initially or the talc within the polymer matrix as appropriate.

The results of the various determinations are given in

Table 1 below which also lists the aspect ratio of the filler before and after mixing with the particular polymer.

TABLE 1

Filler 15% by weight in polymer	Polymer	Particle thickness µm		Filler Aspect Ratio	
		Before Shear	After Shear	Before Mixing	After Shear
Talcs					
Magsil 2628	EVOh	2.62	0.27	6.48	15.48
Magsil Sapphire	EVOh	1.26	0.65	16.94	16.18
Magsil osmanthus	EVOh	2.45	0.31	7.1	26.84
Magsil osmanthus	PET	2.45	0.31	7.1	24.13
Norwegian talc IT Extra	EVOh	0.34	0.19	16.6	16.2
Mica					
Microfine P66	EVOh	0.46	0.37	43.46	33.35
Microfine P66	PET	0.46	0.67	43.46	30.41

It can be seen from Table 1 that for Mica the aspect ratio of the platelets decreases due to the platelets being snapped in the mixing process.

The aspect ratio of two grades of talc, the Norwegian talc and the Magsil Sapphire, remained substantially unchanged by the mixing process, although there is some evidence of delamination.

By contrast the Magsil osmanthus and the Magsil 2628 increased in aspect ratio after processing due to the delamination of the lamellar talc, as also evidenced by the major change in the thickness of the particles. In those

two talcs the reduction in particle thickness is in the order of a factor of 8-10.

The Magsil osmanthus talc showed the greatest increase in aspect ratio after processing and is a high purity talc as is shown by its high CIE index of 56 and its high percentage reflection at 500nm wavelength of about 89.

Example

Pellets made as described above and containing various amounts of Magsil osmanthus were then used to form the core layer of a coextrudate. The coextrudate consisted of a core layer formed from the blend, with a layer of linear low density polyethylene on either side of the core layer. The coextrudate was in the form of a laminated tube for toothpaste tube bodies. The tube consisted of five layers, the two outer layers being of polyethylene and a centre layer being a barrier layer according to the present invention, the two intermediate layers being of a tie polymer to tie the polyethylene layers to the barrier layer. The two outer layers comprising unfilled linear low density polyethylene were 180μm thick, and the barrier layer comprising the blend was 25μm thick. The tie layer comprised maleic anhydride functionalised polyethylene of about 10μm in thickness.

A known weight (about 0.5g) of eucalyptol was introduced into the tube, which was 150mm in length and 35mm diameter with both ends being heat sealed. As a control, a similar and known amount of eucalyptol was sealed into a tube including an ethylene vinyl alcohol barrier layer without any talc present.

The sealed tubes were then stored at 25°C at 40% relative humidity, and the weight loss of the tubes was measured at predetermined intervals. The loss was evaluated as a direct weight loss.

Samples of barrier material were made from ethylene vinyl alcohol (type F101A available from Kuraray) and mixed with talc (Magsil osmanthus) in the weight ratios of:-

1.	EVOh	100:0	Talc
2.	EVOh	90:10	Talc
3.	EVOh	80:20	Talc
4.	EVOh	70:30	Talc

A 25μm thick layer of barrier material was then incorporated in tubes as described above.

After 30 days there was no difference in the weight loss between the different samples. The actual weight loss after 30 days was about 0.005g in all samples, which corresponded with the same weight loss after 5 days for all samples. The slight weight loss may be attributed to both water absorption and loss in the EVOh layers.

CLAIMS

1. A method of making a composition for forming an article having increased barrier to gases and/or vapours, said method comprising the step of mixing together a polar resin with high purity talc filler having a percentage reflectance at 500 nm of at least 85%, the talc filler being capable of delaminating when the composition is subjected to high shear.

2. A method as claimed in claim 1 where the aspect ratio of the filler increases as it breaks down into platelets.

3. A method as claimed in claim 1 or claim 2, wherein the high shear is effected during mixing before the composition is shaped into a finished article.

4. A method as claimed in claim 2 or claim 3 wherein the average aspect ratio of the filler is increased by a factor of at least two.

5. A method as claimed in any one of claims 1 to 4, wherein the talc particles before being subjected to the high shear have an average particle diameter of not more than 20μm.

6. A method as claimed in any one of claims 1 to 5, wherein the filler is a high purity talc having a 50% average particular size of about 17μm, with 70% of the particles having a size of between 10 and 25μm.

7. A method as claimed in any one of claims 1 to 6, wherein the polar resin is one of ethylene vinyl alcohol, polyamide, poly(ethylene terephthalate), polyketone, and poly(butylene terephthalate).

8. A method of making a barrier layer for inclusion in a multilayer construction in which the barrier layer

composition is made by a method as claimed in any one of claims 1 to 7.

9. A composition for forming an article having increased barrier to gases and/or vapours and which is made by a method as claimed in any one of claims 1 to 7.

10. A composition for forming an article having increased barrier to gases and/or vapours, the composition comprising a polar thermoplastic resin filled with a high purity talc having percentage reflection of at least 85% at 500nm.

11. A composition as claimed in claim 10 wherein the filler has an aspect ratio of at least 5 prior to processing.

12. A composition according to claim 10 or claim 11, wherein the polar thermoplastic resin is one of a group comprising ethylene vinyl alcohol, polyamide, poly(ethylene terephthalate), polyketone and poly(butylene terephthalate).

13. A composition according to claim 12, wherein the resin is ethylene vinyl alcohol.

14. A composition according to any one of claims 10 to 13, wherein the platelets of talc have an average size of 2 to 10μm after processing.

15. A composition according to claim 14, wherein the platelets of talc have an average size of 4 to 8μm.

16. A composition according to any one of claims 10 to 15, in which the talc has a percentage reflection of no more than 82% at 380nm.

17. A composition as claimed in any one of claims 10 to 16, wherein the composition contains between 5 and 30% by weight of talc.

18. A laminate article including a barrier layer formed from a composition as claimed in any one of claims 10 to 17.

19. An article according to claim 18 in the form of coextruded tube, or multilayered strip.

20. An article according to claim 19 for incorporation into a toothpaste tube.